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Bio-diesel production and its engine characteristics—An expatiate view

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A B S T R A C T

Nowadays, the awareness about the environment rose among general civic to search for an alternative fuel that could burn with not as much of the pollution. In general, all the vegetable oils are cleaner forms of energy, renewable, and sustainable. So they could be used as an alternative fuel especially in C.I. engines. This review depicts the different methods of bio-diesel production such as transesterification, radio frequency (RF), two-step catalytic process, etc. Subsequently, performance and emissions are two distinct factors that decide the use of fuels in engines; a brief discussion is made on the performance and emission characteristics of various bio-diesel sources like edible oil, inedible orange oil, animal tallow, turpentine oil, waste plastic oil, etc. This paper extends to distinguish exhaust gas recirculation (EGR) from other available methods for NO_x reduction, and finally a comparative evaluation has been made on thermal barrier coated engines with conventional diesel engines.

Contents

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1. Introduction

Petroleum-based fuels are used in almost all sectors of transportation. As the demand of these fuels increases, the price of the fuel also keeps on increasing which has become a great setback for the nation's economy. It is becoming increasingly important to develop sustainable solutions to our energy needs. As fossil fuels are depleting at a faster rate and global warming more heavily affects our lives, the urgency of finding a solution to these problems is more obvious. Energy is considered a critical reason for economic growth, social development, and human welfare. Since their exploration, the fossil fuels continued as the major conventional energy source. With the trend of modernization and industrialization, the world energy demand is also growing at a faster rate. To cope up the increasing energy demand, the majority of the developing countries import crude oil. This puts extra burden on their home economy [1].

The alternative to diesel fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available. Many of these requisites are satisfied by vegetable oils or in general by triglycerides. The problems with directly using vegetable oils are lubrication oil contamination, carbon buildup, etc. Based on the economic aspect, the present market price of vegetable oil is higher than that of diesel. The barriers and interruptions to the bio-diesel production are the availability and wide-spread usage of fossil fuel almost in all places. On the other hand, as a result of developments in oil extraction techniques and agricultural methods, it is expected that in the future the cost of vegetable oils will be getting reduced. In spite of everything, it is possible in certain localities to purchase a number of inedible oils at fairly low prices. Due to the wide variations in soil, climate conditions, and rival uses of agricultural lands, several countries have to think through different vegetable oils as the potential fuels. Each country has to carefully contemplate the type and extent of land for raising such plants [2–4].

Several methods such as preheating, blending, micro-emulsion, pyrolysis (Thermal cracking), and transesterification exist for modifying vegetable oils usable in engines. Among those the most significant is the transesterification method [5]. In C.I. engines the use of bio-diesel reduces CO, HC, PM (Particulate Matter), and smoke, where NO_x increases in most of the cases. The most effective and low-cost technique to reduce NO_x was found to be exhaust gas recirculation (EGR) [6]. Conjointly, the advent of thermal barrier coated (TBC) engines enhanced the performance and emissions when compared to uncoated engines [7]. Based on the above particulars, an endeavor has been made to review renewable bio-diesel technologies across the globe, green field ventures along with the latest innovation, and also to present a clear picture about the current trends in bio-diesel technologies.

2. Historical background

The steps towards alternative fuels were on the go from the invention of the diesel engine by Rudolf Diesel in 1885 onwards. In 1912, he stated, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may in the course of time become as important as petroleum and the coal-tar products of present time" [6–8]. Since the global energy crisis in 1970s substantial attention has been focused on the development of alternate fuels [9]. On the other hand, the oil Gulf crisis in 1973 triggered numerous studies on natural oil and fats all over the world, but the search for alternative fuel has been identified only on 2nd August 1990 [10]. Many researchers and scientists had tried out different types of fuels namely compressed natural gas (CNG), liquefied petroleum gas (LPG), hydrogen, and alcohols. The vegetable oils and alcohols (methanol and ethanol) are favorable renewable liquid fuels. Alcohols are not suitable for diesel engines due to their low cetane number. The poor volatility and low octane number make vegetable oils unsuitable for spark ignition (petrol) engines. One possible solution to this problem is the use of bio-diesel. Straight vegetable oil (SVO) and bio-diesel (which are esters of SVO) are the two fuels which can be used as sole fuel or as mixture along with diesel fuel. Banapurmath et al. [11], Palanisamy and Manoharan [12], Rushang et al. [13], Sharma and Singh [14], Srinivas and Rathanasamy [15], Venkatachalam and Chitra [16], and Hamed et al. [17] reported that the following advantages are noted with bio-diesel:

- Bio-diesel is non-toxic and degrades four times faster than diesel.
- Its oxygen content improves the bio-degradation process.
- Pure bio-diesel degrades 85–88% in water.
- Blending of bio-diesel with diesel fuel increases engine efficiency.
- Bio-diesel has a lower vapour pressure and higher flash point than its petroleum counterpart, making it safer to handle and store.
- Oxygen content of bio-diesel improves the combustion process and decreases its oxidation potential.
- The uses of bio-diesel can extend the life of diesel engine because it has more lubricating property than petroleum diesel fuel.
- Provides a domestic, renewable, and potentially inexhaustible source of energy with energy content close to diesel fuel.
- Bio-diesel obtained from crops produces favorable effects on the environment, such as decrease in acid rain and in the greenhouse effect caused by pollution.
- Bio-diesel is termed as a "carbon neutral" as bio-diesel yielding plants absorbs more carbon dioxide from the atmosphere

during the process of photosynthesis than they add to the atmosphere when used as fuel in compression ignition engines.
- Bio-diesel can be used alone or mixed in any ratio with petroleum diesel fuel.
- Bio-diesel is better than diesel in terms of sulphur content and is generally suitable to match the future European regulations which limit the sulphur content of 0.2% and 0.05% by weight in 1994 and 1996, respectively.
- It helps to reduce a country's reliance on crude oil imports and support agriculture by providing employment and market opportunities for domestic crops.
- The risk of handling, transporting and storing of bio-diesel are lower than petro-diesel.
- The larger reductions in poly aromatic hydrocarbon (PAH) as bio-diesel has no aromatics and no PAH compounds.
- By-product of crude glycerol obtained from transesterification process can be used for manufacturing medical and industrial chemicals.

In contrary, Palanisamy and Manoharan [12], Rushang et al. [13], and Demirbas [18] reported the following disadvantages:

- Higher viscosity.
- Higher copper strip corrosion.
- Slight decrease in fuel economy on energy basics (about 10% for pure bio-diesel).
- Bio-diesel offers unfavorable cold flow properties since it begins to form gel at low temperature which can clog filters or even become so thick that it cannot be pumped from the fuel tank to the engine.
- Density is more than diesel fuel, but may need to use the blends in sub freezing conditions.
- More prone to oxidation than petroleum diesel and in its advanced stages, this can cause acidity in the fuel and form insoluble gums and sediments that can plug filters.
- More expensive due to less production of vegetable oil.

3. Methods for vegetable oil treatment

The main problems associated with the use of vegetable oils are due to their high viscosity and poor volatility. Some methods to overcome these difficulties are

- Preheating.
- Blending.
- Micro-emulsion.
- Pyrolysis (Thermal cracking).
- Transesterification.

3.1. Preheating

Preheating the vegetable oils prior to injection can reduce the viscosity. By preheating the vegetable oils to about 55 °C, the viscosity becomes almost equal to that of diesel. This will improve the spray characteristics of the fuel–air mixture preparation in the engine. Preheated vegetable oils result in improved performance with a reduction in emissions [1,29].

3.2. Blending

A mixture of 10% vegetable oil is used to run the engine without any modifications. At present, it is not practical to substitute 100% vegetable oil in diesel engines, but a blend of 20% vegetable oil and 80% of diesel fuel can be used. Some short-term experiments are conducted with a 50% blend of *Jatropha* oil in diesel engines without any major operational difficulties, but further study is required for the long-term durable operation of the engine. Direct use of vegetable oils and the use of higher percentages of blends of oil have generally been considered not satisfactory for either direct or indirect injection diesel engines. High viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation, polymerization during storage and combustion, carbon deposits and lubricating oil thickening are some of the problems [1,19]

3.3. Micro-emulsions

To solve the problem of high viscosity of the vegetable oils, micro-emulsions with solvents such as methanol, ethanol and 1-butanol had been investigated.

A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions in the 1–150 nm range, formed spontaneously from two normally immiscible liquids. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. A brief study shows that the performance of micro-emulsions of aqueous ethanol in soya bean oil was nearly as good as that of diesel, in spite of lower cetane number and energy content [20].

3.4. Pyrolysis (thermal cracking)

Pyrolysis is the conversion of one substance into another by means of heat in the presence of a catalyst. The pyrolised material can be vegetable oil, animal fats, natural fatty acids or methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world where there is lack of deposit of petroleum.

Many investigators have studied pyrolysis of triglycerides to obtain products suitable for diesel engines. Thermal decompositions of triglycerides produce alkanes, alkenes, alkadines, aromatics, and carboxylic acids [21].

3.5. Transesterification

Transesterification is the process of exchanging the alkoxy group of an ester compound by alcohol and the reaction often catalyzed by an acid or a base. Preheating, direct use and blending, micro emulsion, pyrolysis (Thermal cracking) of straight vegetable oils (SVO) are used only for short-term experiments, whereas transesterification is crucial for producing bio-diesel from bio-lipids for long-term experiments. The transesterification of vegetable oil involves reaction of triglycerides (fat/oil) with bio-alcohol to form esters and glycerol [22].

Many researchers like Makarevicience and Jahulis [23], Tewari [24], and Demirbas [25] reported that the transesterification was achieved with monohydric alcohol (ethanol) in the presence of an alkali catalyst. The previous results show methyl esters to be a suitable replacement for diesel fuel; however, much less has been known about the ethyl esters. So, several studies were carried out to produce the bio-diesel by using ethanol instead of methanol. The chemistry of transesterification for ethanolysis is same as that of methanolysis. The process is also carried out in a similar way that of methanolysis and the catalyst used is alkaline. Methanolysis and ethanolysis of triglycerides are represented in equations (1 and 2) [26].

$$\begin{array}{llcll} CH_2\text{-}COO\text{-}R & CH_3OH & & R\text{-}COO\text{-}CH_3 & CH_2\text{-}OH \\ | & | & & | & | \\ CH\ \text{-}COO\text{-}R & +CH_3OH & \xleftrightarrow{\text{Catalyst}} & R\text{-}COO\text{-}CH_3 & +CH\text{-}\ OH \\ | & | & & | & | \\ CH_2\text{-}COO\text{-}R & CH_3OH & & R\text{-}COO\text{-}CH_3 & CH_2\text{-}OH \end{array}$$

$$\text{Triglyceride} + 3\ \text{Methanol} \xleftrightarrow{Catalyst} 3\ \text{Bio diesel} + \text{Glycerol} \qquad (1)$$

$$\begin{array}{llcll} CH_2\text{-}COO\text{-}R & C_2H_5OH & & R\text{-}COO\text{-}C_2H_5 & CH_2\text{-}OH \\ | & | & & | & | \\ CH\ \text{-}COO\text{-}R & +C_2H_5OH & \xleftrightarrow{\text{Catalyst}} & R\text{-}COO\text{-}C_2H_5 & +\ CH\text{-}\ OH \\ | & | & & | & | \\ CH_2\text{-}COO\text{-}R & C_2H_5OH & & R\text{-}COO\text{-}C_2H_5 & CH_2\text{-}OH \end{array}$$

$$\text{Triglyceride} + 3\ \text{Ethanol} \xleftrightarrow{catalyst} 3\ \text{Bio diesel} + \text{Glycerol} \qquad (2)$$

Based on the above actualities, the various methods (especially transesterification) adopted by researchers for bio-diesel production have been reviewed here.

Singh et al. [27] evaluated the use of magnesium oxide (MgO) impregnated with potassium hydroxide (KOH) as a heterogeneous catalyst for the transesterification of mutton fat with methanol. This process yielded more than 98% of bio-diesel in 20 min. Öner and Şehmus [28] produced bio-diesel from inedible animal tallow by heating tallow between 105 °C and 110 °C before transesterification to remove impurities and bubbles. Metin et al. [29] followed the two-step catalytic process for bio-diesel production from chicken fat with synthetic magnesium (Mg) additive. They used sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) as homogeneous catalysts to improve the reaction rate of bio-diesel and magnesium based additives were used to reduce the pour point, flash point and viscosity of bio-diesel. Efficient bio-diesel production of around 97.7% from beef tallow was achieved with radio frequency (RF) heating conducted by Wang et al. [30]. Marvin et al. [31] discussed about the recovery and pre-treatment of fats, oil and grease from grease interceptors for bio-diesel production. Their study revealed that H_2SO_4 is the most efficient catalyst for reducing free fatty acids to fatty acid methyl esters than $Fe_2(SO_4)_3$ (ferric sulfate). Mehdi and Kariminia [32] prepared bio-diesel from bitter almond oil (BAO). In their investigation 0.9% w/w of KOH concentration produced a maximum yield of 90.8% w/w of bio-diesel. Soletti et al. [33] studied liquid–liquid equilibrium data, tie-lines and phase boundaries for the ternary system canola oil bio-diesel, ethanol and glycerol at temperatures between 303.15 K and 333.15 K in order to overcome the lack of phase equilibrium from the transesterification reaction with ethanol.

The alkaline transesterification of camelina oil using orthogonal experiment (an orthogonal array experimental design (OA16 matrix) is a chemometric method for optimization of methanol-to-oil molar ratio, reaction time, reaction temperature, and catalyst concentration) was studied by Xuan and Leung [34]. In their study, the maximum fatty acid methyl ester yield was around 98.4%. Grisel et al. [35] used (silicon dioxide-hydrofluoric acid) SiO_2-HF solid catalyst for bio-diesel production from *Jatropha*. They reported that 96% of free fatty acid conversion was achieved in their study by using a SiO_2-HF solid catalyst. Rocio et al. [36] produced bio-diesel from marine macro algae. Their process yielded around 1.6–11.5% of bio-diesel. One step alkaline transesterification method for converting moringa fatty acids to their methyl esters was studied by Kafuku and Mbarawa [37]. In their study, an optimal Moringa methyl ester yield of around 82% was achieved. Bari et al. [38] studied the effects of preheating crude palm oil (CPO) and concluded that the viscosity of oil reduced when compared to diesel fuel by preheating it at 92 °C. Hamamci et al. [39] produced methyl esters of peanut by transesterification with methanol in the presence of NaOH as catalyst. Maximum free acid methyl ester yield of around 89% was achieved. The sunflower oil transesterification by using an alkaline catalyst (sodium methoxy) was studied by Schneider et al. [40]. Karnwal et al. [41] prepared bio-diesel from Thumba Oil by transesterification in the presence of potassium hydroxide as catalyst. In their study for 0.75% of KOH concentration maximum ester conversion of 97.8% was obtained. Lin et al. [42] discussed about the bio-diesel production from crude rice bran oil by using KOH as a catalyst. Gürü et al. [43] improved the properties of pomace oil by using synthetic manganese additive, which produced a maximum ester yield of 80%. Haldar et al. [44] prepared bio-diesel from Putranjiva roxburghii non-edible oil by mixing 30% oil with conventional diesel.

4. Properties of vegetable oils

Fuel properties of vegetable oil, methyl esters and ethyl esters of bio-diesel can be grouped conveniently into physical, chemical, and thermal properties. The physical properties include viscosity, density, cloud point, pour point, flash point, boiling range, freezing point, and refractory index. The chemical properties comprise of chemical structure, acid value, saponification value, iodine value, peroxide value, hydroxyl value, acetyl value, overall heating value, ash and sulphur contents, sulphur and copper

Table 1
Physical property of several vegetable oils.

S. no.	Researchers	Name of the vegetable oils	Specific gravity (no unit)	Kinematic viscosity (cSt) @ 40 °C	Calorific value (MJ/kg)	Flash point (°C)	Fire point (°C)
1	Shehata and Abdel Razek [51]	Sunflower oil	0.923	34.2	39.575	274	–
2	Shehata and Abdel Razek [51]	Jojoba oil	0.920	52	39.862	186	–
3	Agarwal and Rajmanoharan [53]	Karanja oil	0.938	35.98	41.66	237	258
4	Sharanappa et al. [56]	Mahua oil	0.924	39.45	37.614	230	246
5	Sing et al. [57]	Waste frying oil and castor oil mixture	0.9231	41.66	37	318	350
6	Hazar and Aydin [60]	Raw rapeseed oil	0.903	31.23	40.112	234	–
7	Venkanna and Venkataramana Reddy [66]	Honne oil	0.910	32.47	39.100	224	–
8	Devan and Mahalakshmi [68]	Neat poon oil	0.9264	49.7	39.650	158	–

corrosions and ignitability of products. Thermal properties are distillation temperature, thermal degradation point, carbon residue, specific heat value, thermal conductivity, etc., [45]. The physical properties of several vegetable oils investigated by the researchers have been compared in Table 1.

It is observed from Table 1 that the fuel properties of vegetable oils are changing from oil to oil. One could observe from Table 1 that the kinematic viscosity of vegetable oil varies in the range of 31–52 cSt at 40 °C. The high viscosity of these oils is due to their large molecular mass. The flash point of vegetable oil is in the range of 158–318 °C. Conversely, the heating values are in the range of 39–40 MJ/kg. The presence of chemically bound oxygen in vegetable oil lowers their heating values by about 10%. This difference may also be due to the amount of carbon chain, triglycerides, and free fatty acids present in the vegetable oils.

Several studies had reported that the characterization of bio-diesel and its blends with diesel demonstrated that almost all the important properties of bio-diesel and its blends are in very close association with the diesel making it a potential fuel for the application in compression ignition engines for partial replacement of diesel fuel. Also, results from several investigations prove that the bio-diesel obtained under the optimum condition is an excellent substitute for diesel fuels. Bio-diesel properties like relative density, viscosity, flash point, cloud and pour points, calorific value, fatty acids contents, quality compound analysis prove that the produced bio-diesel have optimum properties as prescribed in the ASTM standards [45,47,54].

5. Inferences made by researchers

This section describes the performance parameters like brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) of bio-diesel derived from several vegetable oils. The BTE indicates the ability of the combustion system to accept the experimental fuel, and provides comparable means of assessing how efficiently the fuel energy could be converted into mechanical output. On the other hand, BSFC refers to the amount of fuel supplied to engine by the fuel pump on a volumetric basis to maintain the equal energy input to the engine. Also emission parameters like carbon monoxide (CO), hydrocarbon (HC), nitrogen oxide (NO_x), and smoke density of various bio-diesel blends have been reviewed briefly in the subsequent paragraphs.

5.1. *Coconut oil*

Kalam et al. [46] reported that the addition of 30% coconut oil with conventional diesel produced higher brake power (which signifies more useful output power), net heat release rate, and there was an increase in SFC (Specific Fuel Consumption) with increasing coconut oil in blends at constant 50% throttle position with varying speed (800 rpm to 3200 rpm). Exhaust emissions such as HC, smoke, NO_x, CO, and exhaust temperature were reduced with increasing coconut oil in blends. It was inferred that 29% HC, 32% smoke, 16% exhaust temperature, 22% CO and 10% NO_x were reduced by 50% coconut oil blended with conventional diesel fuel. This reduction was due to the O_2 (Oxygen) and lower combustion chamber temperature of 50% coconut oil blend, whereas CO_2 (Carbon dioxide) increased in this study due to the presence of oxygen.

5.2. *Cotton seed oil*

Hüseyin and Hasan [47] observed that the maximum power difference between diesel fuel and diesel–CSOME (Cotton seed oil methyl ester) blends were increased with an increase in the amount of cotton seed oil methyl esters. The BSFC of B20 at full engine speed was found to be lower than diesel fuel. For B50, B75, and B100, minimum CO emissions were observed. However, in the experimental study, the NO_x emissions were decreased for all blends except B5. The reason for this trend was the higher viscosity and lower heating value of cotton seed oil.

Ali [48] conducted an experimental study on a single cylinder, direct injection–type diesel engine using cotton oil soap stock bio-diesel–diesel blends as an alternative diesel fuel. He concluded that the engine power output and engine torque with bio-diesel blends and diesel fuel decreased by 6.2% and 5.8%, respectively. Depending on the amount of bio-diesel and engine speeds, specific fuel consumption values with fuel blends increased by 10.5%.

5.3. *Jatropha oil*

Agarwal and Agarwal [49] prepared bio-diesel from *Jatropha* oil by preheating the oil between 90 °C and 100 °C and blended it with diesel. The performance and emissions tests were carried out at different loads and constant speed (1500 rpm). The optimum fuel injection pressure for diesel and preheated *Jatropha* oil was found to be 200 bar. They observed that the maximum thermal efficiency (30.71%) was found at 200 bar and at 72% of rated load for preheated *Jatropha*, and the lowest BSFC (0.3 kg/kW h) was found at the same pressure and load for preheated *Jatropha* when compared to diesel. The smoke opacity was 42.6%, 41.9%, and 43.6% at 180 bar, 220 bar, and 240 bar, respectively. Overall, the decreased viscosity of preheated oil value was closer to diesel.

Jindal et al. [50] conducted an experimental investigation in a direct injection diesel engine running on *Jatropha* methyl ester and reported that the engine with compression ratio of 18 and injection pressure of 250 bar delivers highest brake thermal efficiency of about 8.2% higher than that of standard settings at full load. It was found that BSFC is always higher for B100 than B20 by about 25–34%.The increases in compression pressure lead

to increase in emissions of HC and exhaust temperature, whereas smoke and CO reduced. The NO_x emissions were found to remain unaffected at higher injection pressure.

5.4. Jojoba oil

In an experimental investigation conducted by Shehata and Abdel Razek [51] on the performance and emission characteristics using jojoba blend indicated higher BTE for pure diesel than B20 at full load conditions due to the higher heating value of diesel and higher BSFC due to the same reason. An increase in CO and CO_2 concentration due to higher carbon/hydrogen ratio and a reduction in NO_x due to lower gas temperature were also observed.

In one more investigation conducted by Salim et al. [52] on improving the performance of dual fuel engines running on natural gas/LPG as the main fuel and jojoba methyl ester as pilot fuel affected the combustion process because of the higher cetane number and higher kinematic viscosity of jojoba methyl esters.

5.5. Karanja oil

Agarwal and Rajmanoharan [53] studied the performance and emissions of Karanja oil and its blends in a single cylinder diesel engine and found that the thermal efficiency of the pre heated oil blends were nearly 30% and for unheated blends it was between 24% and 27% at full load (100%) and at rated speed (1500 rpm) during all experiment. This increased BTE might be due to the reduced viscosity and volatility of oil during pre heating. The pre heated blends also showed an improved trend in the BSFC and BSEC due to increased BTE. The HC emissions from unheated and pre heated blends were lower than that of the diesel due to the presence of oxygen. The NO_x emissions from all the blends with and without pre heating were found to be lower than the diesel fuel at all load conditions. The reason for the formation of NO_x was combustion temperature, the oxygen present in the oil and higher viscosity.

5.6. Koroch oil

Gogoi and Baruah [54] used koroch seed oil methyl ester (KSOME) in a single cylinder diesel engine and reported that the engine BTE at full load for Numaligarh refinery limited (NRL) diesel, B10, B20, B30, and B40 were found to be 25.63%, 24.86%, 24.34%, 24.09%, and 22.32%, respectively. The BTE of various fuel blends was found to be lesser than NRL diesel due to its lower calorific value. Due to higher viscosity and density of KSOME blends, the rate of fuel consumption was found to be more for the methyl esters. Their study revealed the use of KSOME blends up to B30 as fuel for diesel engine without any significant drop in the performance characteristics.

5.7. Mahua oil

Experimental study conducted by Vedaraman et al. [55] on the performance and emission of mahua oil ethyl ester (MOEE) showed a slight increase in BTE (0.06%) when compared with diesel. The rate of fuel consumption increased for MOEE due to its higher density when compared to diesel. Higher cetane number and better combustion of the MOEE proved reduced emissions (CO, HC, $NO_{x,}$ and smoke density) around an average of 58%, 63%, 12%, and 70%, respectively, when compared with neat diesel at 100% load.

Sharanappa et al. [56] tested the performance and emissions of Mahua methyl ester in Cummins, six cylinder, Turbocharged diesel engine and reported that the maximum thermal efficiency was obtained for Mahua methyl ester (B20) than that of diesel. Similarly for the blends B40, B60, and B100, BTE were lesser when compared with diesel, whereas it decreased sharply with a decrease in load for all fuels. The BSFC also decreased with increase in percentage load. CO emissions were found to be lower than diesel and HC emission level reduced from 74 ppm to 50 ppm at the maximum power output of 96 kW. Lower CO and HC emissions were observed in the study due to the complete combustion of MOEE. The NO_x emissions were found to increase with increasing proportion of bio-diesel in blends, which may be due to the increased exhaust gas temperature and more oxygen content in the fuel.

5.8. Mixed oil

In an experimental investigation conducted by Singh et al. [57] in diesel engine using pyrolysis oil from waste frying oil and castor oil mixture showed that the values of BSFC of B10, B30, and B50 at full load were 0.3029 kg/kW h, 0.3617 kg/kW h, and 0.346 kg/kW h, respectively, whereas the values were around 0.394 kg/kW h for diesel. Thus, the decrease in BSFC for bio-diesel might be due to the availability of oxygen in the fuel. Due to complete combustion, there was a decrease in CO by 0.01%, 0.01% and 0.04%, respectively, for B10, B30, and B50 blends when compared to diesel. HC emissions for B10, B30, and B50 at constant engine speed and at full load were 1 ppm, 6 ppm, and 3 ppm, respectively, as compared to 1 ppm of neat diesel. For B10, B30, and B50 blends there was an increase in NO_x of about 11 ppm, 12 ppm, and 10 ppm, respectively, due to higher combustion temperature.

5.9. Orange oil

By using neat orange oil in a C.I. engine an experimental study was conducted by Purushothaman and Nagarajan [58], which showed improvements in BTE of around 3.48% at maximum brake power (4.329 kW) when compared to diesel. This may be due to the better vaporization of orange oil. The values of BSEC (Brake Specific Energy Consumption) were found to be lesser by about 1.4 MJ/kW h with respect to diesel. CO and HC emissions are reduced by 0.2853 g/kW h and 0.0363 g/kW h, respectively, because of lower viscosity of orange oil. Due to the presence of oxygen in the fuel there was an increase in NO_x (1.8 g/kW h) than diesel. The smoke emissions were also reduced marginally for orange oil due to complete combustion and more oxygen present in the fuel.

5.10. Rapeseed oil

Gvidonas and Slavinskas [59] conducted the experimental analysis on DI, four cylinder, four stroke diesel engine D-243(59 kW) with rape seed oil methyl ester (RSOME) as fuel and the parameters like BSFC, BTE, and smoke opacity were analyzed. They concluded that the performance efficiency was nearer to diesel fuel and the emissions were environmental friendly.

Performance and emission evaluation by Hanbey and Hüseyin [60] on a CI engine fueled with preheated raw rapeseed oil (RRO)—diesel blend showed higher brake power for preheated DF and decreased BSFC for preheated RRO50 (50% oil–50% diesel) at maximum engine speed of 2500 rpm. The exhaust gas temperature for preheated RRO20 (20% oil–80% diesel) and preheated diesel fuel were found to be lesser than preheated RRO50. For preheated DF, RRO20 and RRO50, CO emissions were decreased by 20.59%, 16.67%, and 25.56%, respectively. The lowest smoke densities were obtained with preheated RRO50 (26.3%) and RRO20 (20.1%) than with preheated diesel (9.4%). The reason for

this result was due to the reduced viscosity of RRO by preheating it at 100 °C.

5.11. Rubber seed oil

Ramadhas et al. [61] analyzed the performance and emission of diesel engine fueled with rubber seed oil methyl ester (RSOME) and reported that that the maximum BTE obtained was about 3% higher than that of diesel fuel for B10 at the rated speed of 1500 rpm and at maximum load. By using a lower percentage of bio-diesel in bio-diesel–diesel blend the BSFC values decreased. With an increase in bio-diesel percentage, CO emissions were reduced due to the presence of oxygen (11%). Due to complete combustion, CO_2 concentrations were found to be lower for B10 and the smoke density of exhaust emissions were 17% lesser for B20 than that of diesel. It was also inferred that the values of exhaust gas temperature and NO_x emissions are increased in RSOME due to higher engine combustion chamber temperature and oxygen content in the fuel.

5.12. Soybean oil

In an experimental investigation conducted by Qi et al. [62] on combustion and performance evaluation of diesel engine fueled with bio-diesel produced from crude soybean oil, showed higher BSFC for bio-diesel. This higher BSFC was due to the lower heating value of about 10.2% than that of diesel fuel. However, the values of BSEC were found to be closer to that of diesel. CO and HC emissions reduced at full load and load characteristic of 1500 r/min for bio-diesel by an average of 5% and 52% when compared to diesel. The reason for reduction in emission values of CO and HC was due to the presence of oxygen atom in the fuel. An average reduction of NO_x of around 5% due to the difference in engine geometry, compression ratio, less reaction time, and temperature of bio-diesel were also observed in the experimental study.

5.13. Turpentine oil

Saravanan et al. [63] investigated the performance and emission of turpentine oil powered direct injection diesel engine and reported that the BTE was higher for 70:30 diesel fuel/turpentine oil fuel (DF/TPOF) blends due to slightly larger fuel droplets, which resulted in better atomization and complete combustion. The values of specific fuel consumption (SFC) increased for increasing TPOF blends in diesel. It was observed that the exhaust emissions such as HC, CO, PM, $NO_{x,}$ and exhaust temperature of TPOF blends reduced marginally due to the presence of oxygen and better combustion characteristics.

5.14. Waste plastic oil

Mani et al. [64] investigated the characterization and effect of using waste plastic oil–diesel fuel blends and observed higher BTE up to 80% of the load than the diesel fuel. This trend was due to lack of oxygen and higher heat release rate. Emissions such as CO, HC, smoke, and NO_x increased by 5%, 15%, 40%, and 25%, respectively, when compared to diesel.

5.15. Cardonal oil

In an experimental investigation on performance and emission characteristics of double cylinder CI engine operated with cardanol bio-fuel blends, conducted by Mallikappa et al. [65] reported that there was an increase in brake power and BTE with increase in load. This increased BTE might be due to the reduction in heat losses. Brake specific energy consumption decreased (25–30%) at higher brake power. CO and HC emissions were nominal up to 20% blends due to the better combustion of fuel, whereas NO_x emissions in the study increased due to the increased proportion of fuel blends and also with higher exhaust gas temperature (EGT).

5.16. Honne oil

Venkanna and Venkataramana Reddy [66] analyzed the performance, emissions and combustion characteristics of honne oil and found that there was a reduction in BTE of around 4.19% for H100 at full load when compared to neat diesel. CO, HC, and smoke opacity were increased for H100 due to poor volatility, higher viscosity and poor spray characteristics of oil, whereas, NO_x emissions of H100 reduced (117 ppm) when compared with neat diesel due to lower heat release rate of honne oil.

Ong et al. [67] reviewed the production, performance, and emission of palm oil, *Jatropha* curcas, and calophyllum inophyllum bio-diesel and concluded that further research has to be carried out in calophyllum inophyllum.

5.17. Animal tallow

Cengiz Oner and Şehmus [28] experimentally investigated the use of inedible animal tallow as an alternative fuel in a direct injection diesel engine and inferred lower BTE for B5, B20, B50, and B100, also higher BSFC of about 4% (B5), 9.4%(B20), 10.2%(B50) and 15% (B100) at higher engine speed when compared to diesel. The lower heating value of bio-diesel resulted in lower BTE and higher BSFC. Exhaust emissions CO, NO_x, SO_2 (sulphur dioxide) and smoke opacity were reduced for tallow methyl ester around 15%, 38.5%, 72.7%, and 56.8%, respectively. Higher cetane number and shortened ignition delay lead for reduction in emission parameters.

5.18. Poon oil

An experimental investigation of performance, emission and combustion characteristics of poon oil conducted by Devan and Mahalakshmi [68] showed 8–15% higher BSEC and lower BTE when compared to neat diesel at maximum load state and at a constant speed of 1500 rpm, with an injection pressure of 200 bar. CO, HC, $NO_{x,}$ and Smoke emissions reduced by about 12%, 14%, 4%, and 3%, respectively, for B20 poon oil. This reduced engine Performance and emissions were due to high viscosity and lower volatility of neat poon oil.

5.19. Neem oil

Subramaniam et al. [69] investigated the performance and emissions of neem methyl ester in a naturally aspirated direct injection diesel engine at 100% load. Their experimental results showed increases in brake thermal efficiency of around 1.5% for B40 due to the better spray characteristics and dissolved oxygen of B40 when compared to B100 and significant improvements in exhaust emissions (CO, HC, and smoke) due to higher cetane number. However, in the experimental study NO_x emissions increased by 1.03% for B40 due to higher combustion temperature.

6. EGR (exhaust gas recirculation)

Many researchers agreed that EGR is a very effective method to reduce NO_x emissions up to 50–70% in bio-diesel-fuelled engines. A brief review is made on EGR and presented here.

Saleh [70] studied the effects of exhaust gas recirculation on performance and exhaust emissions in a diesel engine operated

with jojoba methyl ester and reported that 50% to 55% of NO_x reduced at 25% to 40% EGR rate above which combustion degraded. The cycle-to-cycle variations (CCV) of the indicated mean effective pressure (IMEP) in a natural gas spark ignition engine with EGR was analyzed by Sen et al. [71]. This showed increased spectral power at 20% EGR level. Qurashi and Boehman [72] discussed about the consequences of exhaust gas recirculation on diesel engine soot and found that soot produced under 0% EGR followed an external burning mode, whereas it followed both internal and external burning modes for 20% EGR.

The various NO_x reduction techniques like use of additives, bio-diesel emulsion with water, retarded fuel injection timing, and exhaust gas recirculation were reviewed and compared by Rajasekar et al. [73].

The impact of simulated EGR on soot reactivity and a laminar co-flow ethylene diffusion flame was studied by Qurashi et al. [74] which showed enhanced soot for simulated EGR compared to real EGR. Pradeep and Sharma [75] conducted an experimental study on diesel and *Jatropha* bio-diesel with and without HOT EGR and inferred reduced NO_x at 15% EGR levels. Agarwal et al. [76] concluded that the simultaneous reduction of NO_x and smoke is possible when both bio-diesel and EGR are employed in C.I. engines.

7. LHR (low heat rejection) engine

LHR engine can be made by ceramic material coatings on the engine cylinder liners, valves, piston, and cylinder head. Many investigations had been carried out with the objective of obtaining higher performance and lower emissions except NO_x with LHR engine, because of higher operating temperature, maximum heat release, and ability to handle the lower calorific value (CV) fuel [7,86]. Performance and emissions of LHR engine compared to commercially cooled diesel engine are presented in Table 2.

It is clear from Table 2 that the coated engine performance and emissions are enhanced than the uncoated engine except oxides of nitrogen, which may be formed due to the higher temperature availability of LHR engine.

8. Conclusion

The review conducted reveals the following information,

- The vegetable oil usually contains free fatty acids, phospholipids, sterols, water, odorants, and other impurities. Because of their presence, the oil cannot be used as fuel directly. To overcome these problems, the oil requires chemical modifications like transesterification, pyrolysis, and emulsification. Among these, the transesterification is an imperative process to produce clean and environment friendly fuel from vegetable oil and it seems to be more suitable because the by-product (glycerol) has commercial value.
- Bio-diesel consists of long-chain fatty acid esters produced by reaction of vegetable oils with short chain alcohols. It is observed that increasing concentration of raw oil, purified oil methyl/ethyl esters in the diesel resulted in the corresponding remarkable increase in kinematic viscosity. A similar phenomenon in specific gravity and flash point are also noted, conversely, a decreasing trend is observed for the calorific value with increasing concentration of oil and esters with diesel.
- Most of the researchers have reported that the BTE of bio-diesel operated engine decreased with increase in bio-diesel–diesel blends. One possible explanation for this trend could be as a result of higher BSFC of bio-diesel due to the presence of fuel-borne oxygen. On the other hand, it is evident from some of the researches that the BTE of pre heated Karanja oil, neat orange oil, and turpentine oil were slightly higher than diesel fuel due to reduced viscosity and better atomization of those oils.
- The high levels of smoke and oxides of nitrogen (NO_x) emissions make the diesel engines difficult to pass through the stern

Table 2
Characteristics of LHR engine compared to diesel engine.

S. no.	Researcher(s)	Fuel used	Coating material	Inferences made
1.	Hazar [77]	Cotton methyl ester	Cylinder head, piston and valves coated with molybdenum (Mo)	Improvement in BSFC (6.0%), emissions (up to 18.0% for CO, 8.0% for smoke density) and increase in NO_x (4.5%).
2.	Hazar [78]	Canola methyl ester	Cylinder head exhaust and inlet valves coated with $MgO–ZrO_2$, whereas the piston surface coated with ZrO_2.	An increase in engine power (up to3.5%), decrease in SFC (4.7 to 8%) and improvement in exhaust emissions except NO_x.
3.	Hasimoglu[79]	Ethanol–diesel fuel blend	Cylinder head, valves, and piston coated with 0.35 mm thick yttria stabilized zirconia ($Y_2O_3–ZrO_2$)	Reduction in NO_x and smoke.
4.	Karthikeyan and Srithar[80]	Ethanol	Cylinder head, piston, exhaust and inlet valves coated with yttria stabilized zirconia ($Y_2O_3–ZrO_2$)	Highest brake thermal efficiency (at 75% load).
5.	Hazar and Ozturk[81]	Corn methyl ester	Piston, cylinder head, exhaust and inlet valves coated with $Al_2O_3–TiO_2$	Improvement in BTE (4.6%) and reduction in SFC and CO (4.7 and 22%) with increased NO_x (8.8%).
6.	Chan and Khor[82]	Diesel	Piston crown coated with yttria-stabilized zirconia (YSZ)	Up to 6% improvement in fuel economy.
7.	Rajendra Prasath et al.[83]	*Jatropha* oil methyl ester	Piston crown, cylinder head, valves and cylinder liner coated with 0.5 mm thickness of partially stabilized zirconia (PSZ)	Increased BTE (1.7%), improvement in SFC (3.77%) and increased NO_x (13.35%).
8.	Murthy et al.[84]	Pure diesel	Air gap insulated piston with 3 mm air gap, with superni crown (an alloy of nickel), air gap insulated liner with superni insert and cylinder head coated with partially Stabilized Zirconia (PSZ)	Increased BTE (7%), Decreased SFC (12%) and increased NO_x (34%).
9.	Mohamed Musthafa et al.[85]	Rice bran and pongamia methyl ester	Cylinder head, cylinder liner, valves, and piston crown coated with nanoceramic Al_2O_3	Improvement in performance and emissions for RME20.
10	HaŞimoğlu et al. [86]	Sunflower oil methyl ester	Cylinder head and valves coated with yttria stabilized zirconia ($Y_2O_3–ZrO_2$)	BSFC increased for bio-diesel (9%) and it decreased for diesel (4%)

emission norms. The high level of smoke emissions is due to the diffusive combustion of diesel engine, whereas oxides of nitrogen emissions are mainly due to high combustion chamber temperature and dissociation. It is very difficult to control simultaneously both the smoke and oxides of nitrogen (NO_x) emission in a diesel engine due to their trade-off.

- Although various methods like use of additives, retarded fuel injection timing, and bio-diesel emulsion with water are available for NO_x reduction, exhaust gas recirculation (EGR) technique was noted to be the most suitable method for reduction of NO_x.
- It is noted that high temperature capability, low thermal conductivity, and the very high fracture toughness of ceramic coatings made it best suited for low heat rejection engine (LHR). With the aid of LHR engine, improvement in BTE, reduction in SFC, HC and CO with increased NO_x by using bio-diesel and its diesel blends were observed by researchers. This may be due to higher operating temperature, maximum heat release, and ability to handle the lower calorific value (CV) fuel.

Energy conservation needs to be a mass movement, once the demand increases, the production increases and the relevant cost will reduce, making renewable bio-diesel energy a viable option. There is a need to conduct further studies on the use of vegetable oils as a substitute to diesel fuel. Based on the present work the future investigations can be made in the following aspects.

- Addition of some anti-freezing additives is needed to improve the cold flow properties of bio-diesel to use it under severe winter conditions.
- Study on oil cake, to process it as fertilizer or to use it as a feedstock for biogas generation.
- Blends of bio-diesel and bio ethanol can be investigated on the various injection timing on diesel engines.
- Measurement of aldehyde emissions can be carried out.

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